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# A Preliminary Analysis of Nitrous Oxide(N20) Including a Materials Balance

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# A Preliminary Analysis of Nitrous Oxide ($N_2O$) Including A Materials Balance

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16. ABSTRACT

This preliminary analysis of the sources, sinks and effect of nitrous oxide ($N_2O$) in the atmosphere is a snapshot in time of a rapidly moving object. Much has been learned about this gas in recent years but much remains to be determined. The most reasonable residence time for $N_2O$ in the atmosphere is in the range 100-150 years. Since the change in atmospheric concentration of $N_2O$ is less than 1% per year, this implies that the release rate is in the range 10-15 Mt $N_2O$/year. The combination of freshwater, ocean and sediment sources appears to be about 7 Mt $N_2O$/year which means that the most that land/crop/fertilizer systems can contribute is 8 Mt $N_2O$/year. The unknown in this balance is the concentration of land/crop/fertilizer systems. Measurement of such fluxes are needed. It appears that the only sinks for $N_2O$ are in the stratosphere. The overall effect of $N_2O$ on stratospheric ozone is predicted to be small and could lead to an increase in stratospheric ozone. The contribution of man made nitrous oxide appears to be small at the present time but is expected to grow. The overall problem is an important one on the time scale 20-50 years and is not an immediate crisis.

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JANUARY 1979

IN HOUSE REPORT

US Environmental Protection Agency
Office of Toxic Substances
401 M St Sw
Washington DC 20460

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## Executive Summary

The Clean Air Act Amendments of 1977 have directed that the Environmental Protection Agency study the effects of and possible control techniques of and other details concerning chemicals that deplete stratospheric ozone. To understand how gases reach the ozone layer, their transport through the troposphere must be determined. The chemical reactions of a gas in all the atmosphere must be known in order to determine the possible effects it may have on stratospheric ozone.

Nitrous oxide ($N_2O$), a gas in the family often referred to as $NO_x$, is produced both naturally and anthropogenically and takes part in the stratospheric chemistry that controls the ozone level. Nitrous oxide appears not to enter into any chemical reactions in the troposphere. The chemistry of nitrogen oxides ($NO_x$) in the troposphere appears to be reasonably well known although more study is indicated for some particular reactions.

The nitrogen cycle requires at one point the fixing of nitrogen from the atmosphere either naturally or industrially. Then either through microbiological action or combustion, the gases NO, $NO_2$, $N_2O$ or $N_2$ may be released mainly through the process of denitrification.

Nitrous oxide appears to be uniformly distributed in the troposphere with a concentration of approximately 310 ppb.

Its lifetime in the troposphere that best seems to fit the models is of the order of 100-150 years.

A number of sources of $N_2O$ are well known but their relative contribution has not been well quantified due to problems of measurement and due to the wide diversity and variability of global sources. Land sources, particularly wet, low pH soils appear to be the largest contributers to atmospheric $N_2O$. The rapidly increasing use of fertilizers represents a source of $N_2O$ that by the end of the century may contribute as much $N_2O$ as do natural sources.

The contribution of nitrous oxide from freshwater sources such as rivers and lakes appears to be small. The relative input from oceans is in dispute although it appears that the smaller estimates are the most likely. Other anthropogenic sources such as fossil fuel combustion may be significant sources but more study seems to be indicated for sources such as fossel fuel plants.

The only well known and proven atmosphere sinks for nitrous oxide are reactions in the stratosphere. It can react with $O(^1D)$ to form NO which depletes the ozone or it can be photolyzed to form $N_2$. Other possible sinks have been suggested but none have been demonstrated as viable alternatives.

It is important to realize that $N_2O$ is part of a natural regulatory cycle involving ozone. The balance of ozone levels depends on the natural creation and destruction of $N_2O$. The effect of human activity may be to upset this balance. A rough idea of the relative contributions of various sources to the atmospheric burden of $N_2O$ can be formed from the data presented in Table I.

Table I

| Sources | Ranges of Values (Mt. of $N_2O$/yr)+ |
|---|---|
| Marine | 5 - 250 |
| land (soil) | 10 - 100 |
| fixed nitrogen including fertilizers* | 6 - 38 |
| man made (direct) | 2 - 6 |
| freshwater | 3 - 40 |
| Total | 34 -474 (a) |

*Fertilizer, represent approximately 1/2 of fixed nitrogen

+Mt. is a million metric tons and is defined in the Appendix

(a) This range of values corresponds to a residence time of 45 - 3.2 yr (53)

Sinks

| | |
|---|---|
| Stratospheric Reactions | 14 - 45 |
| Trospospheric Reactions | 1 - 5 |
| Soil | 0 - 600 |
| | 15 - 650 (b) |

(b) This range corresponds to a residence time between 100 and 2.3 years

As can be seen in Table I the fluxes from sources and sinks do overlap but the range of possible values is so large as to prevent any definite conclusions as to whether other sources (or sinks) exist.

A number of modelers have predicted the possible effects of an increase in atmospheric nitrous oxide concentration (due to anthropogenic processes) on ozone concentration in the stratosphere. See table II for a typical list of reactions used in such calculations. The models include many reactions some of whose rate constants are not well known. Also in some cases the concentrations of the reactants are not well known. Model calculations before 1978 predicted that $N_2O$ increases would have depleted stratospheric ozone by 2023 roughly 5%. However, the present model calculations predict that if $N_2O$ flux is doubled (achievable in the next

50 years) the ozone concentration will only be slightly affected. If $N_2O$ flux is quadrupoled ozone concentration will decrease by 5%. A comparable prediction for the effect of chlorofluorocarbons (CFC) on ozone concentration is a depletion of 20% in the next 25 years at present rates of production.

The problem with respect to CFC's was easy to solve because (a) sources could be readily identified and quantitatively assessed, (b) the stratospheric reactions were well understood, and (c) the solution was easy to implement. None of the above is true for the ozone-nitrous oxide cycle.

It is often argued that if a problem is not a crisis then its study can be postponed. Such an attitude leads to poor planning, inadequate study and understanding of the mechanism involved and sometimes ineffectual control procedures. The $N_2O$ problem could well become such a crisis and with a moderate effort over the next ten years a possible crisis may be averted.

To study the effect of $N_2O$ on stratospheric ozone requires researchers from a wide variety of disciplines. If a coordinated long term and moderate effort to determine, measure and assemble the diverse pieces of information concerning $N_2O$ and its relationship to stratospheric ozone is not pursued, the likelihood of a crisis appears good.

A number of recommendations have been made for future studies. From the present snapshot in time of this rapidly moving object it can be concluded that the problem could be a serious one but it is not an immediate crisis.

## I. Introduction

The Clean Air Act Amendments of 1977 directed, among other things, that the Environmental Protection Agency should study the state of knowledge and the adequacy of research efforts to understand the effects of all substances, practices, processes, and activities which may affect the stratosphere, especially ozone in the stratosphere. Most of the ozone in the atmosphere is found in the stratosphere and protects the earth by absorbing much of the incoming solar radiation in the wave length range 290 to 320 nm that contribute to DUV (biologically damaging ultraviolet radiation sometimes referred to as BUV or erythemal).(1)

The balance of ozone concentration is affected by the amount of various gases entering or formed in the stratosphere. The most important of these gases are the oxides of hydrogen ($HO_x$), the oxides of chlorine ($ClO_x$) and the oxides of nitrogen ($NO_x$). The compounds $NO_x$ include mainly NO, $NO_2$, $N_2O_5$, $N_2O$ and $HNO_3$ which are produced directly by fossil fuel combustion, high flying aircraft or by the interaction of microorganisms in soils, oceans, freshwaters and as a result of the use of fertilizers. $NO_x$ is sometimes referred to as odd nitrogen.

Other mechanisms may also deplete the ozone layer. For example, metals on fine aerosol particles, traces of which may

or may not be catalytically active are a potential ozone depletor. Research is actively going on in this area.[1] Other possible ozone depletors include among others, most of the nonfluorinated halomethanes.

Models of chemical-kinetic reactions and transport for chemicals which directly or indirectly interact with ozone have been developed which consist of a set of mathematical equations. Most current models involve about 100 chemical interactions, many interrelated with each other (see for example table II and reference 2). Due to limitations of computers, most of the models are only one dimensional (altitude). One development from modeling is the realization that the major chemical, catalytic cycles cannot be studied separately. The models do include the parameters of strength of sources, rate coefficients of chemical and photochemical reactions, and mixing coefficients as a function of altitude. They also include absorption coefficients for solar radiation and quantum yields (fraction of light that leads to decomposition) with respect to wave length. Even with all this sophistication the picture is not complete. What is needed is a 3-D model that includes chemical kinetic reactions and more precise and complete measurements of the parameters of the model.

Gases such as $N_2O$, F-11, F-12 and others can absorb thermal radiation in the infrared region of the electromagnetic spectrum and this may lead to a greenhouse effect such as that for $CO_2$.

Table II

CHEMICAL EQUATIONS - THERMAL REACTIONS

(Reference 67)

$O + O_2 + M = O_3 + M$

$O_3 + NO = NO_2 + O_2$

$N_2O + O(^1D) = N_2 + O_2$

$N + O_2 + NO + O$

$O(^1D) + H_2O = 2OH$

$O_3 + OH = HO_2 + O_2$

$O_3 + HO_2 = OH + 2O_2$

$H + O_2 + M = HO_2 + M$

$HO_2 + HO_2 = H_2O_2 + O_2$

$OH + NO_2 + M = HNO_3 + M$

$H_2O_2 + OH = H_2 + HO_2$

$N + NO_2 + N_2 + O$

$NO + HO_2 = NO_2 + OH$

$OH + OH = H_2O + O$

$NO_2 + O_3 = NO_3 + O_2$

$OH + OH + M = H_2O_2 + M$

$^+O + CH_4 = OH + 2HO_2 + CO$

$O(^1D) + M = O + M$

$Cl + OClO = 2ClO$

$Cl + NO_2 + M = ClNO_2 + M$

$ClO + O = Cl + O_2$

$O + O_3 = 2O_2$

$O + NO_2 = NO + O_2$

$N_2O + O(^1D) = 2NO$

$N + NO = N_2 + O$

$^+O(^1D) + CH_4 = OH + 2HO_2 + CO$

$O + OH = O_2 + H$

$O + HO_2 = OH + O_2$

$O_3 + H = OH + O_2$

$HO_2 + OH = H_2O + O_2$

$OH + HNO_3 = H_2O + NO_3$

$N_2 + O(^1D) + M = N_2O + M$

$NO + O + M = NO_2 + M$

$H_2 + O(^1D) = OH + H$

$N + O_3 = NO + O_2$

$^+OH + CH_4 = H_2O + 2HO_2 + CO$

$H_2O_2 + O = OH + HO_2$

$CO + OH = H + CO_2$

$Cl + O_3 = ClO + O_2$

$^+Cl + CH_4 = HCl + 2HO_2 + CO$

$Cl + ClNO_2 = 2Cl + NO_2$

$NO + ClO = NO_2 + Cl$

$ClO + O_3 = Cl + O_2 + O_2$

$ClO + NO_2 + M = ClONO_2 + M$

$ClO + ClO = 2Cl + O_2$

$OH + HCl = H_2 + Cl$

$O + OClO = ClO + O_2$

$N + OClO = NO + ClO$

$Cl + OH = HCl + O$

$Cl + HNO_3 = HCl + NO_3$

$^*CF_2Cl_2 + O(^1D) = 2Cl$

$Cl + H_2O_2 = HCl + HO_2$

$^*CH_3Cl + OH = Cl + H_2O + HO_2$

$NO_2 + O + M = NO_3 + M$

$NO_2 + NO_3 + M = N_2O_5 + M$

$N_2O_5 + O = 2NO_2 + O_2$

$O(^1D) + O_3 = 2O_2$

$ClO + O_3 = OClO + O_2$

$ClO + ClO = Cl + OClO$

$HCl + O(^1D) = Cl + OH$

$O + HCl = OH + Cl$

$NO + OClO = NO_2 + ClO$

$H + OClO = OH + ClO$

$Cl + HO_2 = HCl + O_2$

$^*CFCl_3 + O(^1D) = 2Cl$

$Cl + H_2 = HCl + H$

$ClONO_2 + O = ClO + NO_3$

$NO + NO_3 = 2NO_2$

$NO_2 + NO_3 = NO + O_2 + NO_2$

$N_2O_5 + M = NO_2 + NO_3 + M$

$N_2O_5 + H_2O = 2HNO_3$

$HO_2 + HO_2 + H_2O = H_2O_2 + O_2 + H_2O$

## CHEMICAL EQUATIONS PHOTOLYSIS REACTIONS

$O_2 = O + O$

$O_3 = O(^1D) + O_2$

$N_2O = N_2 + O(^1D)$

$HNO_3 = OH + NO_2$

$HO_2 = OH + O$

$HCl = H + Cl$

$ClO = Cl + O(^1D)$

$OClO = ClO + O$

$^*CFCl_3 = 3Cl$

$O_3 = O + O_2$

$NO_2 = NO + O$

$NO = N + O$

$H_2O_2 = 2OH$

$ClONO_2 = ClO + NO_2$

$ClO = Cl + O$

$ClNO_2 = Cl + NO_2$

$^*CF_2Cl_2 = 2Cl$

$^*CCl_4 = 4Cl$

$^{*}CH_3Cl = 2HO_2 + CO + Cl$

$NO_3 = NO + O_2$

$H_2O = H + OH$

$N_2O_5 = 2NO_2 + O$

$NO_3 = NO_2 + O$

*Products such as F, $H_2$, CO, $COF_2$ etc. are not followed when produced from halocarbons.

+Methyl radical production assumed to yield $2HO_2 + CO$

Although the understanding of the possible effects on climate are not fully understood, an estimate can be made of the magnitude. Using a one-dimensional model [2a] it has been predicted that if the atmospheric concentration of $CO_2$ were to increase by 25% the global temperature would increase by 0.79°K. If the concentration of $N_2O$ were to double after a period of several years the global temperature would increase by 0.68°K.

## II. Troposheric $NO_x$

Atmospheric or air chemistry for $NO_x$ involves two major regions, the troposphere and the stratosphere, where the kinds of chemical reactions that occur are different. In the troposphere, gases are well mixed and homogeneous. This region is shielded by stratospheric gases, mainly ozone and water vapor which absorb much of the ultraviolet light from the sun. As gases move away from the Earth the altitude increases and the temperature generally drops until a reversal occurs, primarily due to the absorption of ultraviolet photons. The position of the reversal is called the tropopause and it is the dividing line between the troposphere and the stratosphere. In the stratosphere the mixture of gases is nonuniform and in general residence times are long if the possibility of chemical reaction is excluded.

A major chemical characteristic of $NO_x$ is their oxidative nature as compared to $SO_x$ which are reductive. This leads to the primary deliterious effect of the $NO_x$ cycle in the troposphere which is often called smog or photochemical oxidations. Photochemical smog involves the input of nitric oxide, sunlight and hydrocarbons. The kinetic chemical reactions that occur in the troposphere involve such intermediate as $NO_2$ and PAN (see figure 1). These reactions have been studied since the 1950's when this problem manifest itself on a significant level in Los

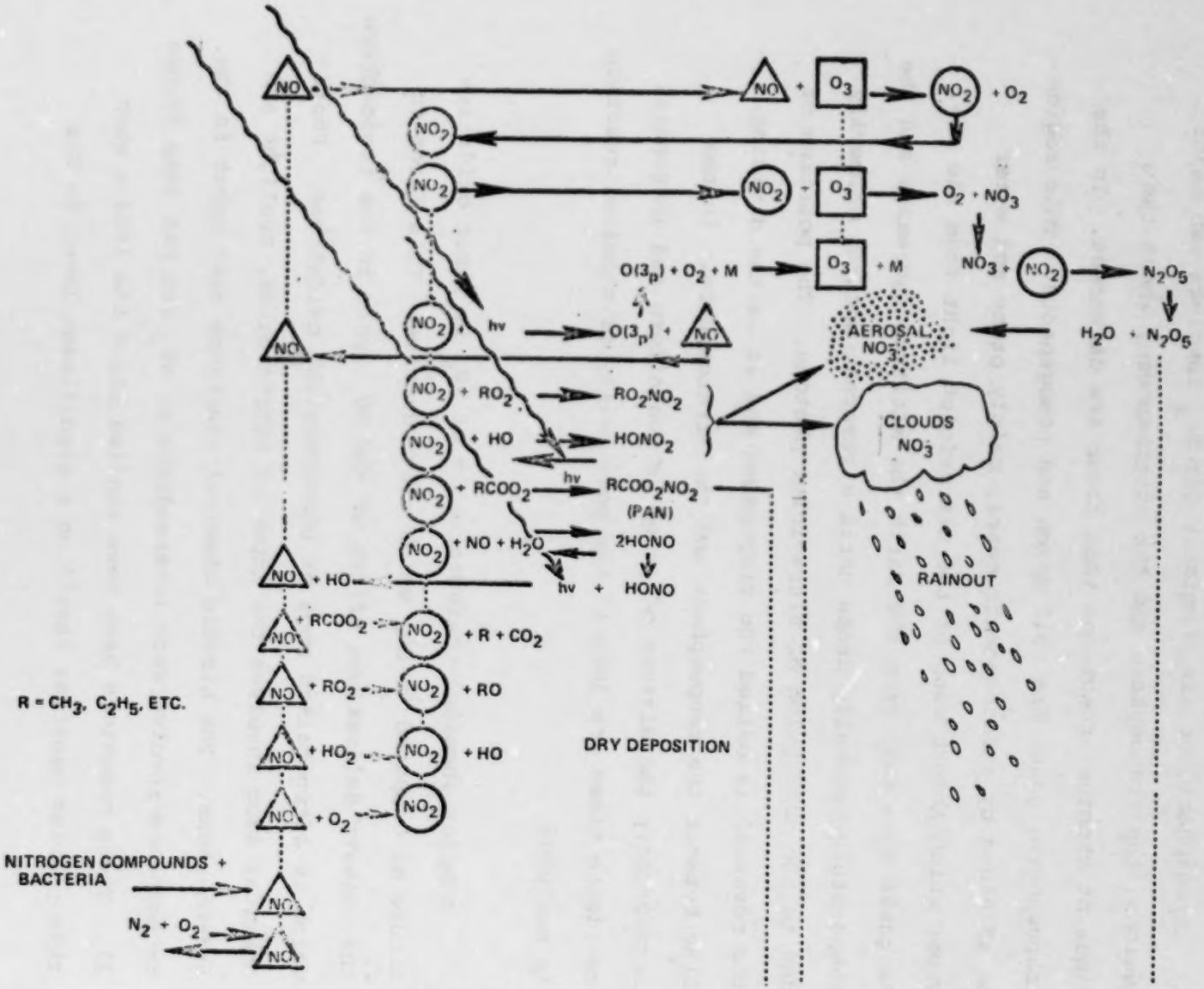



Figure 1 Simplified schematic description of $NO_x$ chemical kinetics in the troposphere. Although not inclusive of all possible detail, the main pathways can be seen.

Angeles.[3] It has been demonstrated that the chemical compounds involved vary in concentration throughout the day depending on the amount of sunlight and input gases. The intermediates are the compounds responsible for eye irritation, adverse respiratory effects, plant damage and the browning of the atmosphere known as smog.[4] Some of the color is due to adsorption of sunlight by the intermediate products and some is due to polymerizing of the oxidation products forming aerosols.

The two major nitrogen oxide constituents in the atmosphere are NO (nitric oxide) and $NO_2$ (nitrogen dioxide). The major oxide, NO is produced by the high temperature combustion process in the presence of $N_2$ in the air. Some $NO_2$ is produced by lower temperature 300°K oxidation. The amount produced is dependent more on the concentration of NO than $O_2$ in the reaction.

$$2NO + O_2 \rightleftharpoons 2NO_2$$

As seen in figure 1 nitric oxide reacts commonly with the oxidizing agents such as the transient hydroperoxyl ($HO_2$), alkylperoxyl ($RO_2$) and acylperoxyl ($RCOO_2$) free radicals. In these reactions R represents methyl ($CH_3$), ethyl ($C_2H_5$) and higher alkyl groups.

Nitrogen dioxide plays a very central role in tropospheric chemistry being involved directly or indirectly in virtually every kinetic pathway. It reacts with water and nitric oxide to form nitric and nitrous acids in the reactions;

$$2\ NO_2 + H_2O \rightleftharpoons HONO_2 + HONO$$

and

$$NO_2 + NO + H_2O \rightleftharpoons 2\ HONO$$

And as shown in figure 1, $NO_2$ finds a sink in the reactions with HO, $RO_2$ and $RCOO_2$. If R = $CH_3$ then the latter reaction involves PAN ($CH_3COO_2NO_2$) or peroxyacylnitrate. This compound is the mysterious compound X of the 1950's involved in photochemical smog.

A source of ozone in photochemical smog involving $NO_x$ follows from the photodissociation of $NO_2$;

$$NO_2 + h\nu\ (<4300\ \mathring{A}) \longrightarrow O(^3P) + NO$$

followed by;

$$O(^3P) + O_2 + M \longrightarrow O_3 + M$$

The ozone is either quickly ozidized by NO or photolyzed to produce HO;

$$O_3 + h\nu \longrightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \longrightarrow 2HO$$

The oxidation of $NO_2$ by $O_3$ leads to the production of $N_2O_5$ which forms on aerosol or reaches the ground by dry deposition. As shown in figure 1 the acids fromed by $NO_2$ also form aerosols and become part of the clouds eventually reaching the ground by rain out.(5)

It is generally concluded by researchers of kinetic chemical reactions in the troposphere that the major reactions and pathways are now "reasonably well" understood.(5) However some reactions have been recommended for future studies.

One major area requiring further study is the reaction of longer chain $RO_2$ with NO and $NO_2$ as a function of temperature and pressure. The chemistry of PAN, particularly for higher analogues such as PPN need to be investigated. Particularly information is required concerning thermal decomposition.

The reactions of $NO_3$ that require further investigation are;(5)

$$NO_3 + NO \longrightarrow 2\ NO_2$$

$$NO_3 + NO_2 \longrightarrow N_2O_5$$

$$NO_3 + h\nu \longrightarrow NO + O_2$$

$$\longrightarrow NO_2 + O$$

as well as the reaction

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

In summary, $NO_x$ tropospheric chemistry involves some mechanisms which require further study. Besides those mentioned above research is needed in areas such as aerosol production (heterogenous chemistry) and acid rainfall. However those processes that are related to chemicals involved in ozone depletion appear to be well enough known that the major attention should be focused on what happens in the stratosphere and how the chemicals that get there are produced.

## III. STRATOSPHERIC $NO_x$

### A. Introduction

As shown in Table III the $NO_x$ catalytic cycle is a major cause of depletion of stratospheric ozone. One of the gases involved in stratospheric $NO_x$ chemistry that is of concern with regard to ozone depletion is nitrous oxide ($N_2O$).

TABLE III

Approximate mechanisms for the Depletion of Stratospheric Ozone [6] (average for the region from 25 to 40 km in altitude).

| Mechanism | Percent of $O_3$ destruction rate |
|---|---|
| Photolysis | 20 |
| Transport to the Troposphere | 0.5 |
| Hydroxyl and Hydroperoxyl Radicals | 10 |
| $NO_x$ Catalytic Cycle | 50-70 |
| $ClO_x$ Catalytic Cycle | 10-40 |

As with many of the atmospheric reactions which interrelate different chemical cycles, the $ClO_x$ and $NO_x$ cycles are so related. For example, chlorofluoromethane decomposes by photolysis

in the stratosphere releasing chlorine which consumes ozone by the reaction;

$$Cl + O_3 \longrightarrow ClO + O_2$$

But the abundance of ClO may be influenced by

$$ClO + NO \longrightarrow Cl + NO_2$$

and by

$$ClO + NO_2 + M \longrightarrow ClNO_3 + M$$

and

$$ClO + HO \longrightarrow HO_2 + Cl$$

Nitrous oxide is produced naturally by microbial action on any nitrifiable substance and from anthropogenic sources among which are fertilizers and burning of fossil fuels. It has been used as an anesthetic and for that use has been called laughing gas.

A recent Study[66] suggests that nitrous oxide (laughing gas) may have some direct toxicological effects on anesthesiologists and dentists. This conclusion is based on largely

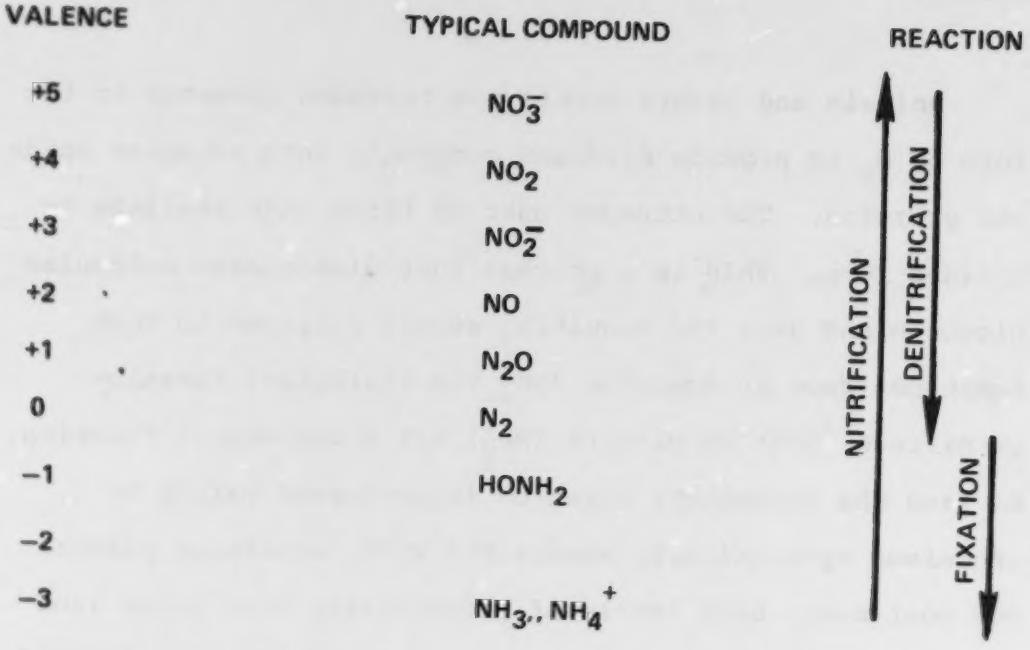



Figure 2 Relationship between nitrification, denitrification and fixation as they relate to valence and compound (reference 42).

circumstantial evidence. However there is some evidence that the gas increases the fetal death rate and may cause leukopenic effects.

Animals and plants cannot use nitrogen directly in the form of $N_2$ to produce nitrogen compounds such as amino acids and proteins. The nitrogen must be first made availabe in a fixed form. This is a process that dissociates molecular nitrogen and uses the resulting atomic nitrogen to form compounds such as ammonium ($NH_4^+$ via biological fixation or nitrate ($NO_3^-$) or nitrite ($NO_2$) via a biological fixation. On land the biological fixation is performed mainly by organisms symbiotically associated with leguminous plants. For continuous high levels of productivity over large land areas fertilizer must be used, but high yields over limited areas on a continuous basis or on extensive areas intermittently can be obtained by recycling biologically fixed $N_2$. In aqueous media fixation is primarily accomplished by blue-green algae.

Nitrous oxide can in principle be produced by either nitrification or denitrification. Nitrification is the microbial oxidation of ammonia to nitrate and nitrite. Biological nitrification is the major source of $N_2O$ in the biosphere, and is mediated primarily by obligate aerobic bacteria.

Denitrification is carried out by bacteria that can use nitrate as a terminal electron acceptor when oxygen has been depleted via the sequence;

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

| nitrate | nitrite | nitric oxide | nitrous oxide | molecular nitrogen |
|---|---|---|---|---|

(see also figure 2)

The above sequence is somewhat oversimplified. For example, it appears that between $NO_2$ and $N_2O$ is an intermediate sometimes referred to as X.[2] It is possible that X is hyponitrous acid but the present evidence is not positive and no identification can be made at this time. It has been estimated that about 25-30% of the time does fixed nitrogen go into denitrification in soils[65] and about 6% in oceans.

The ability of soil microorganisms to reduce $N_2O$ to $N_2$ is inhibited by the $NO_3^-$ content of the soil.[62] All nitrogen fertilizers provide nitrate to the soil, either directly, because they may be wholly or in part in the nitrate form, or because they are in the ammonium form or are changed to the ammonium form, which can then be converted to nitrate. All crop management inputs and techniques which increase plant growth and return

more plant biomass to the soil and increase the amount of nitrate produced in the soil.

Without the denitrification process the oxygen and nitrogen of the atmosphere would long ago have been depleted. Thus one would expect that the rate of denitrification is on the average equal to the rate of fixation.

As long as there is sufficient free oxygen the aerobic microorganisms use it for respiration. However when the oxygen level falls below 5% in soils the microbial population may use both free oxygen and combined oxygen in the form of nitrate thus forming $N_2O$. Since $N_2O$ is a gas, some of it in any case will diffuse away before the denitrification becomes complete. Under the situation of extreme lack of oxygen, $N_2O$ will be an intermediate with $N_2$ the final product. It is thus important to measure the $N_2O/N_2$ ratio in the denitrification process for different ecosystems.

Factors that affect denitrification are; [6,10]

1. Free oxygen content must be very small (e.g. in soils, water, sediments). The redox potential should be 330 mv.[65]

2. The temperature range must be between $5^0C$ and $60^0C$, although individual species have narrower acceptable temperature ranges.[11]

The production rate usually follows the well known Arrhenius equation with rate changing expedientially with temperature.

3. When the pH is lower than 6.5 generation of $N_2O$ compared to $N_2$ is favored[12] although the total denitrification rate is decreased.[9]

4. There must be an available carbon source.

B. Atmospheric Concentration and Residence Time

In the troposphere up to 12 km the concentration of $N_2O$ is fairly constant. However there is some disagreement about the absolute value of the concentration. Hahn and Junge [13] put the value at 260 ppb while Singh et. al. [14] find it to vary less than 4% between northern and southern hemisphere at an average concentration of 311± 2.6 ppb. A recent urban study puts the value at 329.5± 3.35 ppb.[15] The value has been shown to increase 1.5% over the last decade by Weiss & Craig and 0.3%/yr for the last two years by Singh et al.[14] However the latter experimenter observes that they could not detect a change if it were less than 0.5%/yr. Some researchers using the above information claim that there is no $N_2O$ problem.[17] From balloon measurements[58] the change of $N_2O$ concentration is less than 1%/yr.

An early study of $N_2O$ concentration [48] showed a concentration increase of roughly 20 ppb/yr during the period 1967-1969. An extrapolation of this increase would predict the 1978 atmospheric concentration to be roughly 460 ppb. Since the concentration is nowhere near this high and since the data has not been reproduceable it is highly suspect.

According to Tony Brodrick[46] and Paul Crutzen[47] there is no convincing hard evidence that the concentration of $N_2O$ is changing in the atmosphere. Crutzen feels that the study by Weiss is "coming close" but he feels that additional data are needed.

In the troposphere the concentration thus is approximately 310 ppb and decreases to about 50 ppb at 35 km. This leads to a tropospheric burden of $M = 1.6 \times 10^{15}$ gm.* A similar calculation for the stratosphere leads to an additional burden of $0.16 \times 10^{15}$ gm. Using an average removal or residence time of $T = 80$ yr. then the input flux to the troposphere is;

$$Q = \frac{M}{T} = \frac{1.6 \times 10^{15} \text{ gm}}{80 \text{ yrs.}} = 20 \times 10^{12} \text{ gm of } N_2O/\text{yr.}$$

* This value can be arrived by using the information that $1 \text{ m}^3$ of air = 1.2 kg at ground level and approximately 0.4 kg at 12 km. Then let the average mass density for the troposphere = mixing ratio (by volume) of $N_2O$ X average density of the troposphere X volume of the troposphere = $(310 \times 10^{-9})$ $(0.8 \text{ kg/m}^3)$ $(\frac{4}{3}\pi)$ $\left[(6412)^3 - (6400)^3\right] \text{ m}^3 = 1.6 \times 10^{15}$ gm. of $N_2O$.

Uncertainties still exist concerning the value of the tropospheric residence time of $N_2O$. A method for estimating residence time ($\tau$est) has been described by Junge, Let; [18]

$\sigma_a$ = real standard deviation (for concentrations)

$\sigma_t$ = overall standard deviation

$\sigma_p$ = variability due to precision

then $$\sigma_a^2 = \sigma_t^2 - \sigma_p^2$$

Quantitatively Singh et al[14] finds these values to be

$$\sigma_a^2 = (0.8)^2 - (0.3)^2 = (0.7)^2$$

Then using the general Junge criterion

$$\tau\text{est} = \frac{14}{a} = 20 \text{ years}$$

It seems surprising that any meaningful value emerges from this analysis since $\sigma$ is a quantity that has a subjective component. This relationship seems to hold for several atmospheric gases. However it is not clear how the real standard deviation is extracted from the data or if that is possible. The wide variation of non local effects also contribute to the uncertainty of the determination of this value.

It has been observed[52] that Junge's model represents a valid lower limit for lifetime. Other modelers put the lifetime at, 150 yrs[60] 130 years[52] and 100 years[53]. These are lifetimes with respect to stratospheric photochemical destruction. Thus they are upper limits and other sinks could shorten the photochemical lifetimes. Note that if the variability is less than 1% in the troposphere this is consistent with a lifetime larger than 100 yrs.

Some authors use different names for this quantity. For instance Singh et al.[14] determines the turnover rate to be 67 years. The term removal rate is sometimes used.[18] If a gas is consumed the description used is lifetime but if the gas is merely passing through to the stratosphere perhaps a better description is residence time.

Crutzen and Ehhalt[8] note that in 1967-68 there was a sharp increase in $N_2O$ levels indicating that the turnover rate must be "short". Using Junge's relationship described above they get $\tau_{est}$ = 10 yrs with an uncertainty of a factor of two.

The estimates of the residence time of $N_2O$ range from 5 to 160 years.[13] It appears that a more reasonable range of possiblities is 100-150 years.

The equation used above, M = QT shows that far a given burden M, Q and T are not independent.[7] Using the known concentration of $N_2O$ as shown above led to $1.6 \times 10^{15}$ gm. It would appear that atmosphere concentration is know within an accuracy of 10%. Thus M is the best known quantity in the equation. The above range of residence time (100-150 yrs) has a larger uncertainty. This range of lifetimes implies an injection rate of between 16 and 11 Mt $N_2O$/yr.

## C. Sources of $N_2O$

### 1. Land

#### a. Review

The denitrification losses in soils depends on a number of factors among which are the availability of organic carbon substrate, the moisture content of the soil ($0_2$ content or redox potential), the presence or absence of a cover crop and the type of fertilizer applied. The proportion of nitrogen liberated as $N_2O$ varies from 0 to 100%. Another example of wildly varying fluxes is shown in the fact that the $N_2O/N_2$ ratio can vary between 1/0.06 and 1/6. [9]

There are three main methods used to measure fluxes of nitrous oxide from the soil, viz;

1. use soil profile concentration measurements and classical molecular diffusion theory (e.g. reference 20,21,22)

2. the box method measuring how concentration changes with respect to time (27,68,69)

3. the micrometeorological method which applies turbulent diffusion theory to air concentration profiles (24).

Example of fluxes of $N_2O$ that have been measured from soil using the profile method generally are of the order of magnitude of $10^{-12}$g cm$^{-2}$ s$^{-1}$ of $N_2O$ ($3.4 \times 10^{-12}$ g cm$^{-2}$ s$^{-1}$ for soil covered with grass and trees to less than $0.1 \times 10^{-12}$g cm$^{-2}$ s$^{-1}$ for desert soil). Cropland soils show fluxes of approximately $0.3 \times 10^{-12}$gm cm$^{-2}$ s$^{-1}$. Compost piles show concentrations as high as 20 ppm.(15)

As an example of the third method one worker uses the aerodynamic profile method which calculates fluxes using the equation;(19,24)

$$F = K^2 V_*^2 \ (C_2 - C_1) \ / \ (u_2 - u_1)$$

where

$$V_* = \frac{U_*}{k} \quad \frac{U_2 - U_1}{\ln[(Z_2 - d) / (Z_1 - d)]}$$

$F$ = flux density ($gm/cm^2/sec$)

$K$ = von Karman's constant (0.41)

$U^*, V_*$ = friction velocity (cm/sec)

$C$ = $N_2O$ concentation ($gm/cm^3$) at height, $Z$(cm)

$u$ = windspeed (cm/sec) at height $Z$ (cm)

$d$ = crop height (cm)

The method does allow correction for thermal instability.

Using the above method one experimenter has determined that $N_2O$ can emanate or be absorbed by soil. His calculations for two separate days showed a flux towards the soil of $\sim 230 \times 10^{-12}$ gm $cm^{-2}s^{-1}$ on a warm dry day call a flux of $\sim 160 \times 10^{-12}$ gm $cm^{-2}s^{-1}$ on a colder damper day.

These values are surprising in two ways. First they are considerably larger than most other measurements (a recent study shows that the concentrations change by as much as an order of magnitude in one day[15]) and secondly they show that in one case the soil is a sink. The method used is the closest to a direct measurement but it does depend on a theoretical model. One possible explanation of the large fluxes calculated in this way is that in general the fluxes are both in and out of the soil and that those experimentally measured by the first

two methods is the difference between the emitted and absorbed fluxes. A recent estimate indicates that the $N_2O$ supplied to the atmosphere by soils probably does not exceed about 7 M tons N/yr.[63]

b. Analysis

To understand the magnitude of a flux from soil of magnitude 100 gm $cm^{-2}$ $s^{-1}$ consider the situation where 2/3 of the global land mass (1/3 the earths surface area) is emitting at that rate;

$$100 \times 10^{-12} \frac{gm}{cm^2\ sec}\left[\frac{3.15 \times 10^7\ sec}{1\ yr.}\right]\left[\left(\frac{2}{3}\right)\left(\frac{1}{3}\right) 4\pi(6400)^2\ km^2\right]\left[\frac{10^{10} cm^2}{1\ km^2}\right] = 3000\ Mt\ N_2O\ per\ year$$

This can be compared to the total global soil nitrogen loses due to agricultural activites of 6000-13000 MT.[23] This is larger than the total flux from all sources estimated as 210 Mt/yr earlier. This is clearly much too large a flux and suggests that the problem is more complex than has previously been expected. It also demonstrates the danger of extrapolating from a single site to a global level.

Evidence for the complexity of the relationship between $N_2O$ and soil is shown in a study of Iowa surface soils showed that their capacity for uptake of $N_2O$ under conditions favor-

able for denitrification of nitrate was much greater than their capacity for the release of the gas.[26] The experiments involved incubating the soils in anerobic conditions and showed that the soils had the capacity to take up all the $N_2O$ produced by denitrification. At least 90% of the gas released was in the form of $N_2$. This information casts doubt on techniques used to measure the flux of $N_2O$ which rely on soil concentration profiles and indicates that the use of chambers placed over soil surface is a superior technique.[6]

An upper limit on the flux of $N_2O$ possible from any system is given by the rate of fixation. In some cases the rate of fixation is known more precisely than the rate of $N_2O$ emission. From some "very patchy" evidence[23] it is estimated that nitrogen fixation occurs in forests to the extent of $3\text{-}5 \times 10^{-12}$ gm $cm^{-2}$ $s^{-1}$. For an area of global forests of about $4.1 \times 10^9$ ha ($1ha = 10^8 cm^2$) or $4.1 \times 10^{17} cm^2$ this gives a global average of approximately 50 Mt/yr nitrogen fixed in forests. A similar analysis for unused land yields $\sim 0.6 \times 10^{-12}$ gm $cm^{-2}s^{-1}$ for $4.9 \times 10^9$ ha and a global total for nitrogen fixed of 10 Mt/yr.

The emission and absorption of $N_2O$ by soils is the most diverse and complex part of the situation and would thus deserve the most attention and investigation in the future (note also in the section and sinks that soils could be a very large sink for $N_2O$).

In summary, although some experimental measurements have been made to determine the $N_2O$ levels for soil systems they are too few and specialized to make accurate generalizations from. Studies need to be made involving several parameters among which should be; type of ground cover, kind and amount of cultivation, moisture and humidity, pH, meteorological conditions, sunlight, fertilizers or nutrient and soil composition. The measurement of $N_2O$ from land areas will likely be the most difficult complex and involved of any of the natural flux determinations.

## 2. Freshwater and Sediments

### a. Review

As recently as 1977 no known measurements had been made for fresh waters.[13] However recently it has been shown that fresh surface water is supersaturated with $N_2O$ bearing about 20% more than the air immediately above it.[19] Significantly larger concentrations supersaturated by factors up to five have been found by Cicerone et al which are due to anthropogenic activities such as sewage treatment.[27] Also municipal tap water samples from U.S. cities show saturation factors between 1.8 and 89.2 (a factor of one indicates equilibrium and a factor of 89.2 means that the dissolved $N_2O$ was 89.2 times more concentrated than in equilibrium with the atmosphere).

It was suggested that chlorination of river water and wastes might be a key step in the production of $N_2O$.

Within a few cm. of the surface of sediments exist the ideal denitrification condition. A possible mechanism for nitrate transport involves the upward seepage of groundwater. Estimates for the amount of nitrogen denitrified by this process range from 23 to 81% of that retained in the lake.[16]

In lakes it was found that only waters deeper than 100 ft. produced significant amounts of $N_2O$.[19] It is suggested that this occurs since photoplankton are absent and the supply of organic matter is scarce. In these circumstances the nitrifying microorganisms can compete more successfully for the limited amount of available ammonium. Also there are often more nutrients below the discontinuity layer (50-60 M) than in surface water.[13]

b. Analysis

The average flux from some lakes is approximately $2 \times 10^{-12}$ gm $cm^{-2}$ $s^{-1}$).[6] It might be expected that the average flux from fresh water sources would be of this order of magnitude but slightly higher. Using $2 \times 10^{16} cm^2$ as an estimate of the area of freshwater and $5 \times 10^{-12}$ gm $cm^{-2}$ $s^{-1}$ as a rough estimate of the average flux of $N_2O$ from freshwater sources than the annual flux would be:

$$5 \times 10^{-12} \frac{gm}{cm^2\ sec}\left[2 \times 10^{16} cm^2\right]\left[\frac{3.15 \times 10^7}{1\ yr.}\right]\left[\frac{1\ Mt}{10^{12}\ gm}\right]$$

$$= 3.15\ Mt\ of\ N_2O/yr.$$

Some heavily polluted rivers such as the Rhine show fluxes as large as $70 \times 10^{-12} gm\ cm^{-2} s^{-1}$.(28)

It has been suggested that $N_2O$ is produced in water and soil systems by the oxidation (nitrification) of ammonia in addition to that produced by denitrification. If this is so monitoring $N_2O$ could be used as a way to study nitrification.

Thus the contribution from freshwater sources appears to be small however it would appear that a more careful and closer examination should be made of the contribution of sewage treatment plants.

3. Oceans

Nitrification appears to take place in the soil, water, the upper layers of sediment and in the ocean where it is most efficient below 200 M. Hahn and Junge(13) suggested that this occurs since photoplankton are absent and the supply of organic matter is scarce. In these circumstances the nitrifying microorganisms can compete more successfully for

the limited amount of available ammonium. Also there are often more nutrients below the discontinuity layer (50-60M) than in surface water.

The range of fluxes measured from oceans vary widely. These fluxes are not measured directly but involve using concentration data with a model. The most common model is called a stagnant film diffusion model[13] or a two layer model.[29] The model assumes that both phases (air and sea) are well mixed and that there is no turbulence or wind. The flux is then proportional to the difference between the concentration of $N_2O$ in the water and the water concentration when in equilibrium with the atmospheric abundance. This is derived from the one dimensional relationship for molecular diffusion.[29]

$$F = - D \frac{\partial C}{\partial Z}$$

where F is the flux, c the concentration, Z the depth and D the coefficient of molecular diffusion of gas in the layer (air-sea layer). The rate of evaporation/condensation determines the exchange parameters. The proportionately factor in the above relationship can be derived for ideal conditions.

Measurements of 42 ocean samples from the North Atlantic by Hahn and Junge[13], some taken at depths of 3000 m, show

a concentration of $N_2O$ in the water of 0.4 ppm v. Some of the samples were slightly below equlibrium concentration and some were saturated by as much as 280%. The flux using the above simplified model is 70 Mt $N_2O$/yr for all the oceans if the average concentration is 0.4 ppm v. The individual flow ranged from (0.82 to 1.66) x $10^{-12}$ g $cm^{-2}s^{-1}$ near the equator to (0.05 to 0.66) X $10^{-12}$ g $cm^{-2}s^{-1}$ at 60 degrees north latitude.

The global number was determined by substitution in the relationship.

$$F = - K (C - Ceq)$$

where C = 0.4 ppm v was the concentration found on the water and Ceq = 0.25 ppm v was the assumed equilibrium value (Ceq is actually closer to 0.31 ppmv).

Singh et al[14] have measured water concentrations in the Pacific ocean with an average surface saturation of 133% (a super saturation of 33%). They found that some of the concentration below the mixed layer to vary between 1 and 7 times that of the surface concentration. These values lead via the model to an oceanic flux of 0.359 x $10^{-12}$gm $cm^{-2}s^{-1}$ or 32.4 Mt $N_2O$/yr. If fresh water sources are included the total goes up to 35 Mt $N_2O$/yr.

A survey was made of several oceans of the world sampling $N_2O$ in the surface water and the air by Weiss et al.[30] Each day analysis was made of the atmosphere and the ocean for a total of approximately 8000 analysis in all. They were analyzed by gas chromotagraphy with a precision of 0.3 to 0.4%.

The trip covered the ocean from California through the Panama Canal to Spain, then through the Mediterranean Sea to the Arabian Sea, and Mauritius. The trip then went to Antartica and Australia.

The overall average super saturation of ocean waters with respect to the atmosphere was approximately 4% with a few occasional spikes as much as two fold. These values are much lower than those of Hahn and Junge.[13]

The procedure used to determine the flux from the ocean was to determine the partial pressure of $N_2O$ and then estimate how much was released. A check is provided in the levels of radon gas released from the radium in sea water. The atmosphere has very little natural radium). This mechanism will show the rate of release of a gas from the ocean.

In general the saturation levels were very near the equilibrium level except in regions where there is upwelling

bringing $N_2O$ up from the lower depths or frontal boundaries formed by sharp temperature changes.

Contrary to the findings of Hahn and Junge[13] and Singh et al[14], the levels found by Weiss[30] in the North Atlantic were remarkably uniform and averaged no more than a few percent from saturation. The western basin of the Mediterranean showed some supersaturation and the Red Sea was slightly undersaturated. But as samples were taken further south in the Red Sea values they showed significant spikes. These high values correlated well with oceanic mixing boundaries. The highest value of the expedition of two fold supersaturation was recorded at one point in this area.

The Northern Arabian Sea showed isolated high values of 320-330 ppb due to upwelling. In the Antartic a polar front structure reflected $N_2O$ distribution. This is a region where warm water is moving one way on one side and cold water another way on the other side.

Using the above concentrations, the model, and the radon flux information a global flux estimate can be made. This estimate assumes that the tract followed by Weiss was representative of all the ocean. The estimate of approximately 4 Mt $N_2O$/yr and is considerably lower than the 70 Mt $N_2O$/yr estimated by Hahn & Junge.[13] Due to the major differences in measurements in the

ocean and their importance (see discussion in Global Balance $N_2O$ section) the magnitude oceanic fluxes needs to be measured by an independent researcher. In terms of biological activity the surface of the oceans over the world is very heterogerous. Hahn, Weiss & Singh have simplified different parts of the large and highly variable ocean.

## 4. Fertilizers

### a. Review

The dramatic increases in crop yields since WW II have been largely due to an increased use of nitrogen fertilizers and plant nutrients. This has been mainly due to better genetic stock. Higher yielding hybrids require more nutrient and care; therefore, the agricultural chemicals become very important in allowing the plants to reach their genetic potential.

The mechanism by which $N_2O$ is produced usually involves an anerobic bacterial activity denitrification. It is estimated that about 1/3 of fertilizer used (57 Mt was fixed industrially in 1974-reference 23) in agriculture is returned to the atmosphere by denitrification in a relatively short time (decades or so). The yield of $N_2O$ from fertilizers is between 5 and 20%. Thus the fertilizer used may end up as nitrous oxide although it may take several years for this to happen. The time estimates of this phenomena show a large range of uncertainty.

Commercial fertilizers are made up of nitrogen in the form of nitrate, ammonium, and/or organic nitrogen compounds. They are used to fertilize arable soil and in some cases on pasture land. They add to the substrate to enhance denitrification and nitrogen uptake.

Different chemical forms of a fertilizer added to the soil can lead to $N_2O$ production.[13] If it is added in the form of a nitrate the mechanism of denitrification may follow and if it is added in the form of an ammonium it will follow a cycle of bacteria nitrification leading from $NH_3$ to $NH_2OH$ and the intermediate X.[13,31]

If fertilizers are added to the soil in the form of urea they are hydrolyzed by soil urease to form $(NH_4)_2\ CO_3$. It was observed that this ammonium is nitrified under aerobic conditions to form nitrate. The amount of the resulting $N_2O$[31] released can be greatly reduced by the use nitropyrin. However, this has not been demonstrated under field conditions.

High $N_2O$ fluxes are found immediately after a rain or in anerobic conditions. Using $NaNO_3$ produced fluxes of 50 x $10^{-12}$g $cm^{-2}$ $s^{-1}$ for recently cropped areas after a rain,[13] and applying $KNO_3$ has yielded fluxes of up to 480 x $10^{-12}$g $cm^{-2}$ $s^{-1}$. This latter flux was 10 days after application.

The $N_2O$ flux increased until the 18th day when it reached $1350 \times 10^{-12}$ g $cm^{-2}$ $s^{-1}$. Thus $N_2O$ can be generated by the anerobic denitrification of nitrate fertilizer. However the values were determined by the soil gradient technique and thus are questionable.

b. Analysis

An estimate can be made of $N_2O$ flux from fertilizers by assuming that each person on earth requires 1/2 acre for food production ($4 \times 10^9$ people and 1 acre = 0.004 $km^2$). Using a flux of $10^{-11}$ gm $cm^{-2}s^{-1}$ produces 25 Mt $N_2O$/yr from fertilizers.

The contribution of fertilizer usage to atmospheric $N_2O$ appears to be the largest anthropogenic source and should be expected to increase significantly in the future.

5. Other Anthropogenic Sources

a. Review

The relationship between natural and anthropogenic $N_2O$ is demonstrated by comparing the natural rate of fixation with that due to industry. The natural rate of nitrogen fixation is about 200 Mt/yr.

Industrial fixation for agricultural purposes was 3.5 MT/yr. in 1950 and it is predicted to be between 100 and 200 Mt/

yr. (the rate of application of nitrogen fertilizer in 1977 was about 40 Mt.)[8,23] by the end of the century.[28] It is estimated as 79 Mt/yr.[16] For all other industrial processes the rate was 15 Mt/yr in 1950, 40 Mt/yr in 1974 and could grow to 100 Mt/yr by 2000. These values should be compared to the natural rate of about 160 Mt/yr. Thus it can be seen that the rate of $N_2O$ released from anthropogenic sources could be growing at a rapid rate.

As pointed out earlier the concentrations of $N_2O$ can be larger near wastewater treatment plants.[27,28] This occurs in part because the easiest and most economical way to treat wastes involves nitrification followed by denitrification. It is the latter step that produces nitrous oxide.[32]

Samples of air had been taken, sealed and kept from as far back as 1961 by Harman Craig of the Scripps Institute of Oceanography.[30] They have been analyzed for $N_2O$ and the concentrations show a slow statistically significant increase with time. They go from 291 ppb in 1961 to 300 ppb in 1978. This increase is very similar to that of $CO_2$ for the same time period. For the last decade the $N_2O$ atmospheric concentration has increased 1.5%[16] while that of $CO_2$ has increased 2%. It suggests from these measurements that the $N_2O$ change in the atmosphere may be anthropogenic.

Samples from the exhaust stacks fossil fuel power plants have been taken and analyzed for the $N_2O/CO_2$ ratio. The $CO_2$ concentration value is well known for combustion processes being in the range 12-14%. The exhaust stack concentrations of $N_2O$ for two large fossil fuel plants were 25.8 and 25.0 ppm by volume. The equilibrium values are of the order of 0.1 ppm showing concentrations of least two orders of magnitude above equilibrium. It was suggested that the major source of $N_2O$ in the stack is from the reduction of NO

$$4NO \longrightarrow N_2O + N_2O_3$$

This was substantiated by the fact that NO was present at about 1/10 of its equilibrium value in the stack. The mechanism involved here is a mystery at present.[53]

The data showed a considerable variability and it has since been suspected that this is due to catalytic destruction of $N_2O$ by surface adsorption at high temperatures.[30] More recent measurements show the $N_2O/CO_2$ ratio to be in the range $1.5\text{-}2.7 \times 10^{-4}$. Using an average $CO_2$ value of 12% this leads to a range of $N_2O$ in exhaust stacks of 18-32 ppm by volume.[30]

These concentrations when combined with the world wide coal and oil consumption figures lead to an estimate of the contribution of combustion to $N_2O$ global flux of 1.6 Mt $N_2O$/yr. Crutzen and Enhalt[8] using the data of Picrotti and Rasmussen put

the value at 2.2 Mt $N_2O$/yr. It is also predicted that this flux is increasing at a rate of 3.5% per year.

It has been suggested that the use of catalytic converters could lead to the production of $N_2O$ by the reactions;[2]

$$6NO + 4NH_3 \longrightarrow 5\ N_2O + 6H_2O$$

and

$$2NO + H_2 \longrightarrow N_2O + H_2O$$

b. Analysis

The $N_2O$ in automobile exhausts was found to be less than ambient levels unless catalytic converters were used and then the concentration was found to be in the range of 1-10 ppm by volume.[16,15] Using an average value of 6 ppm for the concentration of $N_2O$ from autombiles their contribution to the global flux can be estimated. Assume that there are 100 million automobiles with an average engine displacement of 2 liters running at 2000 rpm for 2 hours each day each with a catalytic converter. Then the total contribution from automobiles would be

$$\frac{2000 \text{ revolutions}}{\text{min}} (2 \times 365 \text{ hours}) \frac{(2000 \text{ cm}^3)}{(\text{revolution})} (6 \times 10^{-6}) \frac{(1.2 \text{ kg})}{(\text{m}^3)} (10^8)$$

$$= 0.13 \text{ Mt } N_2O/\text{yr}$$

Thus the contribution from automobiles would be minimal even with the catalytic converters.

Thus there are several anthropogenic sources other than fertilizer usage that need further study. Possible significant contributions can be made by fossil fuel combustion and sewage treatment processes.

## D. Sinks of $N_2O$

### 1. Stratospheric Sinks

Once $N_2O$ survives long enough to reach the stratosphere it has two possible sinks[2]

$$N_2O + O(^1D) \longrightarrow 2NO \qquad K = 6.3 \times 10^{-11}$$

$$\longrightarrow N_2 + O_2 \qquad K = 5.1 \times 10^{-11}$$

Stratospheric $N_2O$ can be destroyed by photolysis

$$N_2O + h\nu \longrightarrow N_2O + O$$

The resulting nitric oxide is an ozone depleter

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad K = 2.1 \times 10^{-12} \exp(-1470/T)$$

The meaning of a rate constant (unit $cm^2$ $molecule^{-1}$) is found in the relationship

$$\tau = \frac{1}{kc}$$

where $\tau$ is the lifetime, k the rate constant and c the concentration.

The amount of $N_2O$ consumed by the reaction

$$N_2O + O\ (^1D) \longrightarrow 2NO$$

$$K = 6.3 \times 10^{-11} \qquad \frac{cm^3}{molecule}$$

can be determined using the following information

| Altitude (km) | $O(D^1)$ from reference (45) particles/$cm^3$ | Atmospheric $N_2O$ Mixing Ratio ppb(v) from reference 13 | $\underline{N_2O}$ Atmospheric denisty-from reference (45) (particles/$cm^3$) |
|---|---|---|---|
| 20 | 1 | 180 | $1.7 \times 10^{18}$ |
| 25 | 6 | 100 | $7.7 \times 10^{17}$ |

| | | | |
|---|---|---|---|
| 30 | 30 | 70 | $3.6 \times 10^{17}$ |
| 35 | 100 | 40 | $1.7 \times 10^{17}$ |
| 40 | 330 | 10 | $8.1 \times 10^{16}$ |
| 45 | 700 | - | $4.3 \times 10^{16}$ |
| 50 | 60 | - | $2.3 \times 10^{16}$ |
| 55 | 45 | - | $1.3 \times 10^{16}$ |
| 60 | 300 | - | $7.2 \times 10^{15}$ |

Then using the relationship

$$\frac{-d[N_2O]}{dt} = K[N_2O]\ [O(^1D)]$$

| Altitude (km) | $[O^1D)]$ (particles/$cm^3$) | $[N_2O]$ | $K[O(^1D)]\ [N_2O]$ molecules/$cm^3$/sec |
|---|---|---|---|
| 20 | 1 | $3060 \times 10^8$ | 19.3 |
| 25 | 6 | $770 \times 10^8$ | 29.1 |
| 30 | 30 | $252 \times 10^8$ | 47.6 |
| 35 | 100 | $63 \times 10^8$ | 42.8 |
| 40 | 330 | $8.1 \times 10^8$ | 16.8 |

The volume of a spherical shell at these altitudes with a width of 5 km is = $2.6 \times 10^9$ $km^3$.

Thus we have at 20 km for example:

$$19.3 \frac{\text{molecules}}{\text{cm}^3 \text{ sec}} \left[2.6 \times 10^9 \text{ km}^3\right] \left[\frac{10^{15} \text{cm}^3}{1 \text{ km}}\right] \left[\frac{44 \text{ gm}}{6 \times 10^{23} \text{ molecules}}\right] \left[\frac{3.15 \times 10^7 \text{sec}}{1 \text{ yr}}\right]$$

$$- \quad (19.3) \ [6.0 \times 10^9] \ \frac{\text{gm}}{\text{yr}}$$

$$= 11 \times 10^{10} \ \frac{\text{gm}}{\text{yr}} \longrightarrow 2NO$$

then add the contribution for all altitudes

$$(19.3 + 29.1 + 42.8 + 16.8) \quad (6.0 \times 10^9) \ \frac{\text{gm}}{\text{yr}} =$$

1.0 Mt $N_2$0yr/ for consumption to form N0

also 1.0 Mt/yr to the reaction producing $N_2$ and $0_2$

Thus most of stratospheric $N_2$0 must be photolyzed in order to have an overall sink of the order of 20-40 Mt $N_2$O/yr. in the stratosphere.

Most of the estimates of the strength of the sink for $N_2$O with $0(^1D)$ fall around $1.0 \times 10^8$ molecules $cm^{-2}s^{-1}$. (25) A more recent value using Crutzen's 2D model is $5.1 \times 10^8$ molecules $cm^{-2}$ $s^{-1}$. These lead to annual values of 1.2 Mt $N_2$0/yr and 7 Mt $N_2$0/yr.

Crutzen[33] estimates that $3.4 \times 10^9$ molecules/cm$^2$/sec of $N_2O$ cross the tropopause at 15 km and are either photolyzed or react with $O(^1D)$. This latter reaction returns $2.5 \times 10^8$ molecules/cm$^2$/sec of NO, $NO_2$ and $HNO_3$ back to the troposphere. The net result is that $3.1 \times 10^9$ molecules/cm$^2$/sec are consumed in the stratosphere. This corresponds to consumption of approximately 33 Mt of $N_2O$/year in the stratosphere.

Recently reactions in the stratosphere involving $HO_2$ have been investigated in some detail and new rate[34,67] constants and temperature dependence has been determined. This new information indicates that $HO_2$ consumes NO faster than had been previously thought. Thus some of the stratospheric NO produced from $N_2O$ will deplete $HO_2$ rather than $O_3$.

A recent NASA report[35] puts the rate coefficient for $N_2O + ClO$ at less than $10^{-12}$ exp (-4260/T) and states that the reaction rate for photolysis in the troposphere as negligible. Thus the most common tropospheric reactions have negligible rates for the consumption for nitrous oxide.

However, the consumption of $N_2O$ by photolysis and reaction with the excited state of oxygen remain the only known sinks in the atmosphere of any size.

## 2. Other Possible Sinks

It has been demonstrated that soils may act as sinks as well as sources for $N_2O$ through the uptake of atmospheric $N_2O$ by soil microorganisms.[6,26] This suggested idea has also been suggested as a mechanism involving oceans.[18]

Several possible tropospheric reactions have been investigated. The rate constant for $N_2O + OH$ is less than $4 \times 10^{-16}$ $cm^3$/sec with a corresponding removal time of more than $10^4$ years.[6] The experimental turnover time determined by direct measurement is 5-15 years. A recent report shows the rate constant to be $(3.8 \quad 1.2) \times 10^{-17}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$.

It is suggested that the reactions

$$N_2O + HO_2 \longrightarrow N_2 + O_2 + OH$$

$$\longrightarrow 2NO + OH$$

will be slower than that with OH by factor of 100.

Using the data of Blackmer and Bremner[26] an estimate can be made of the possible magnitude of the soil as a sink. They showed that approximately 1 µg of $N_2O$ can be absorbed by a gm of soil in 10 hrs. This rate was measured for 30 gm

density of roughly 0.6 gm/cm$^2$. Then assuming that 1/6 of the earth is soil and that the radius of the earth is 6400 km the annual absorption of $N_2O$ by solid would be:

$$\frac{1\ \mu g\ N_2O}{gm\ 10\ hr}\left[\frac{0.6\ gm}{cm^2}\right]\left[\frac{24\ hr}{1\ day}\right]\left[\frac{1\ Mt}{10^{18}\ \mu g}\right]\left(\frac{1}{6}\times\frac{1}{4}\right)4\ \Pi\ (6400)^2\ km^2\left[\frac{10^5 cm}{1\ km}\right]^2$$

$$\simeq\ 112\ Mt\ N_2O/yr.$$

Assuming that soil conditions will be appropriate about 1/3 of the year yields on annual absorption of $\simeq$ 40 Mt $N_2O$/yr. This estimate is derived from an enclosed bench top experiment and there is only weak evidence that measurements in the field demonstrate such an effect. (Cicerone showed that on 8 of 60 days his soil was a sink[15] and similar results have been found by Rolston[55] & Piebie.[56] It would seem that before the microorganisms involved in denitrification can consume the nitrates and start consuming the $N_2O$ it is blown away. However in the sense that everything comes from somewhere and goes somewhere the $N_2O$ transported by the wind could be absorbed at another site. Recent diurnal variations in $N_2O$ atmospheric concentrations found by Bruce, Eggleton and Penkett[43] suggest that there is an important ground surface sink for $N_2O$. This uptake appears to be due to the reduction of $N_2O$ to $N_2$.[44]

It has been shown that nitrous oxide will undergo both a thermal and a photochemical decomposition at 296°K when it is absorbed on various dry sands.[51] The rate of decomposition was dependent on pressure and moisture. The destructive efficiency under optimum conditions was the order of $2 \times 10^{-5}$ molecules/incident photon. Assuming that 1/3 of the global land mass is desert or near-desert and 1.7% of solar intensity is in the range 280-320 nm then approximately 70 Mt/yr of nitrous oxide could be consumed at the above rate. Thus decomposition by desert soil is a potential sink for $N_2O$.

Thus although some possible sinks for $N_2O$ in the atmosphere other than photolysis and reaction $O(^1D)$ have been suggested, none has been definitely shown to be a viable mechanism.

## IV. Global Mass/Materials Balance of $N_2O$

In analyzing a complex system such as the way that nitrogen and its compounds move through the environment the mass or materials balance approach can be a useful organizational tool. This model examines all possible sources and sinks allowing the comparison of different fluxes of $N_2O$. It also provides insight and understanding into seemingly unrelated components, flows between reservoirs, the relationships between anthropogenic and natural sources and allows for a better design of monitoring on data gathering activities.

However the data regarding fluxes of $N_2O$ are somewhat limited and have a large uncertainty. For example the amount of $N_2O$ evolved from land was estimated as being between 16 and 69 Mt N/yr by one research group based on only two experiments. And recently it has been shown that the soil could be a sink of the order of 60 Mt $N_2O$/yr. This wide range of values makes it very difficult to predict the effect on the stratosphere due to $N_2O$. To get a rough of the order of magnitude of global flux units assume that the average global production of $N_2O$ is $1 \times 10^{-12}$ gm $cm^{-2}$ $sec^{-1}$. Then for the earth:

$$1 \times 10^{-12} \frac{\text{gm}}{\text{cm}^2 \text{ sec}} \quad 4\,\Pi \left[(6400)^2 \text{ km}^2\right]\left[\frac{3.15 \times 10^7 \text{ sec}}{1 \text{ yr.}}\right]\left[\frac{10^5 \text{ cm}}{1 \text{ km}}\right]\left[\frac{1 \text{ Mt}}{10^{12} \text{ gm}}\right]$$

= 160 Mt $N_2O$/yr is emitted into the atmosphere

The global net production of $N_2O$ is estimated by others to be between 125 and 475 million metric tons (Mt) of $N_2O$ per year with 210 Mt as the most likely value.[13] A recent review[13] listed the estimates for sources and sinks of $N_2O$. These and other values are shown in Table IV.

TABLE IV

| Sources | Amount ($10^6$ metric tons of $N_2O$/yr) Likely value | Range |
|---|---|---|
| Marine | 70 (5)[a] | 5-250 |
| land (soil) | 25 | 10-100 |
| fixed nitrogen including fertilzer | 20 | 6-38 |
| man made (direct) | 4 | 2-6 |
| fresh water (13) | 5 | 3-40 |
| Thunderstorms | 10[b] | 8-40[c] |
| Total: | 144 (79) | 34-474 |
| **Sinks** | | |
| Stratosphere; Reaction with UV and $O(^1D)$ | 20 | 10-45 |
| Troposphere; Reaction with $O(^1D)$, OH, negative ions & $HO_2$ | 0 | 0-5 |
| Soil | 23 | 20-40 |
| | | 15-650 |

a) recent measurement by Weiss,[30] b) educated evaluation, c) reference [36]

As can be seen from Table IV a large unknown sink could exist in the atmosphere for $N_2O$. At this time there are some guesses as to what that sink might be e.g., the soil). At least

one researcher has suggested that the above marine estimates are much too large and thus there is no missing sink.[3]

Some controversy centers on how much comes from (or goes to) the oceans. Hahn,[13] Yoshinari[37] and Singh[14] et al have estimated fluxes from oceans that require a tropospheric sink. Singh concludes that since the oceans are so large, the contribution from anthropogenic sources must be small. Weiss[30] with his lower estimate of oceanic flux would say all the sources & sinks are known and balance (his flux value combined with Hahn & Junge's other estimates place the lower bound of sources much closer to estimate value for sinks). Some support for this latter view comes from a review by McElroy et al.[28]

The Marine estimate shown in Table IV comes from an average of the few measurements made over oceans. It would appear that more measurements are needed over oceans. The most important areas are those which are nutrient rich such as the upwelling zone along the West African coast, the Indian Ocean and the Arabian sea, and coastal areas near some rivers connecting to highly populated areas.

One source puts the estimated input of $N_2O$ from fertilizer at 3 to 11 Mt N/yr as the result of a postulated fixation rate

of 200 Mt N/yr. For comparison with Table IV this would be 5 to 16 Mt $N_2O$/yr.[8]

The land estimate range of values in Table IV could also be narrowed by better numbers for the fluxes over crops and forests. Using the data given by Blackmer & Bremmer [26] the estimate of a soil being a sink could be as large as 40 Mt $N_2O$/yr. Thus the soil could turn out to be a significant sink of $N_2O$.

The fertilizer estimate is derived from the amount used and estimate of how much is released. Two projects are underway to start such measurements.[19,38] However, it appears that the precision of 0 ppb can only detect fluxes down to about $10^{-10}$ gm $cm^{-2}$ $sec^{-1}$ which is two orders of magnitude above the flux estimates from soils and water. A recent study claimed that a detection limit for flux of $2 \times 10^{-13}$ gm $cm^{-2}$ $s^{-1}$ can be acheived using samples taken over even 30 minute durations.[39] The discrepancy concerning the possible limits of detection appears to be caused by different sample handling techniques, and the theoretical flux models used.

In summary the estimates of fluxes associated with sources and sinks of $N_2O$ are based on very few actual measurement. They are for the most part rough first order estimates and in some respects are confusing. With some authors suggesting that

the oceans and soil are potential sinks and that the flux may be into and out of these areas indicates that there are many open questions and much more to be learned about how the $N_2O$ cycle works.

A recent estimate indicates that the $N_2O$ supplied to the atomosphere by soils probably does not exceed about 7 M tons N/yr. (63)

A not unreasonable approach to determining the best overall guess from the current inadequate information would be as follows:

1. Use the estimate of $N_2O$ flux that is determined by residence; viz, 11-16 Mt $N_2O$/yr.

2. Assume that all sinks are in the stratosphere and we use the upper limit; viz, 16 Mt $N_2O$/yr.

3. Then assume that freshwater and ocean sources (including sediments) yield 7 Mt $N_2O$/yr. and other sources contribute another 1 Mt $N_2O$/yr.

4. Then on balance land/crop/fertilizer systems must contribute 8 Mt $N_2O$/yr. This could be all due to sources or a combination of sources and sinks.

## II. Effect of $N_2O$ on Stratospheric Ozone

Predictions have been made of the increase in $N_2O$ burden in the atmosphere due to fertilizer use. Assuming a 6% annual increase in the use of fertilizers, the increase by the year 2000 will be between 7 and 31% of the 1975 atmospheric burden of $N_2O$.[13] It is possible that at some future date (approx. 100 yrs) the $N_2O$ production rate will be 3 times what it is now due to anthropogenic sources.[28]

Models have been used to predict the change in stratospheric ozone due to $N_2O$.[6,7,23,40] Using the first order approximation that the rate of nitrogen fixation is the same as that for $N_2O$ production, the % decrease can be calculated as a function of increase in nitrogen fixation.

It has been observed[67] that the interaction of $N_2O$ in the atmosphere and its resulting effect on $O_3$ is non-linear. Fiqure 3 shows the relationship between the multiple of present $N_2O$ release and change in total ozone. However the analysis shown below does give an indication of the variables involved. Since this analysis is only a first order approximation its usefulness is restricted.

Stratospheric $NO_x$ is produced primarily by nitrous oxide and the relationship between $NO_x$ and $O_3$ has been shown to be[7]

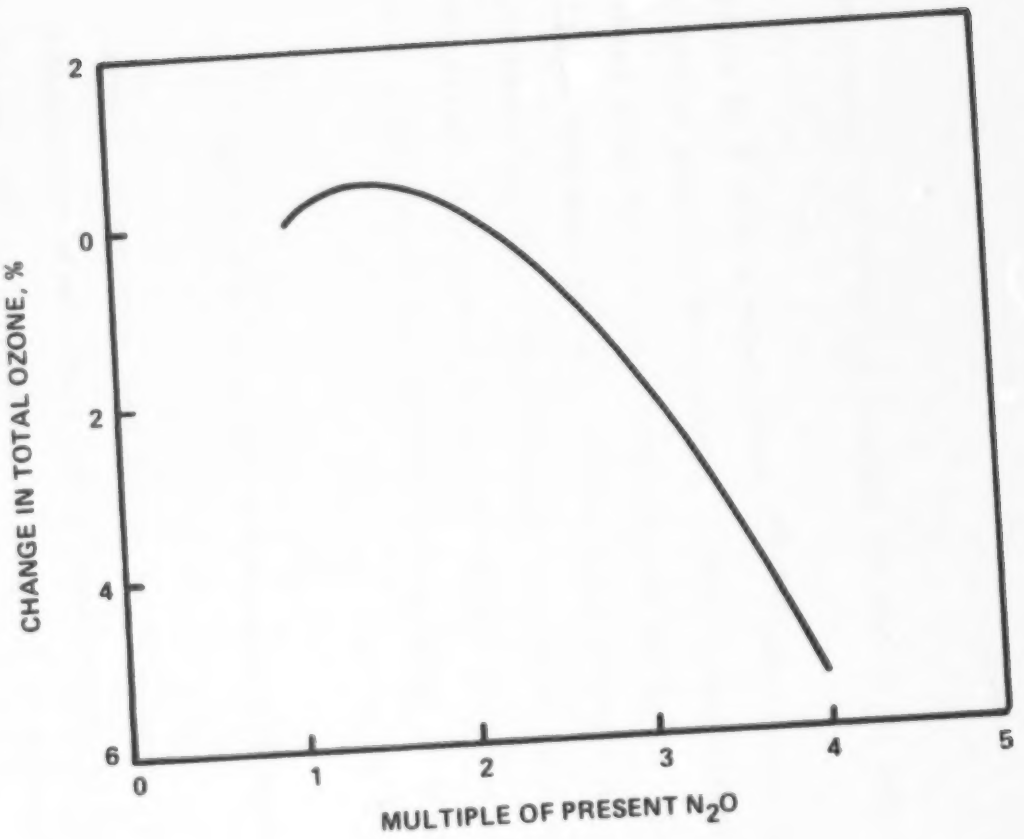



Figure 3 Effect on stratospheric ozone of increases in the present rate of release of $N_2O$ (reference 67).

$$\frac{\Delta[O_3]}{[O_3]} = X \frac{\Delta[NO_x]}{[NO_x]}$$

However since the primary source of stratospheric $NO_x$ is nitrous oxide, then;

$$\frac{\Delta[O_3]}{[O_3]} = X \frac{\Delta[N_2O]}{[N_2O]}$$

where $[O_3]$ and $[N_2O]$ are the amounts of ozone and nitrous oxide.

Recent information[46,64] would suggest that X is quite small and positive (perhaps 1/10). Previous values were in the range -1/5 to -1/10. Thus it is suggested that $N_2O$ actually leads to an increase in ozone concentration. Such assessments should be treated with some caution. There are still some unknowns that could change the value of X. Some key measurements that remain involve methane chemistry, water vapor effects, and tropospheric concentrations of HO.

The main reasons for this recent change in effect are:

1. ClO has more of an effect than previously thought.
2. More NO is consumed by $HO_2$ than previously thought.
3. The ozone is found in 3-D models to be less sensitive to $N_2O$ than previously thought.

The important variables used in the analysis of $N_2O$ mass balance are:

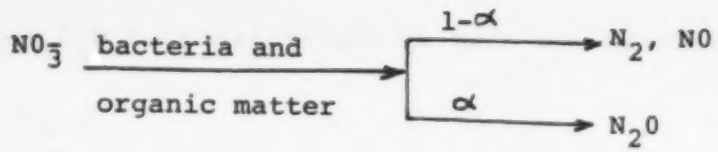
$\Delta N_F$ = The increase in global nitrogen fixation due to human activities (Mt/yr) (from combustion, manufacture, and use of fertilizers and cultivation of legumes - this assumes that the major changes are due to human activities)

$\alpha$ = Fraction of denitrified nitrogen that is $N_2O$

$\beta$ = Fraction of fixed nitrogen that is denitrified within a few decades

$\tau$ = Atmospheric residence time of $N_2O$

Of the estimated 200 to 350 Mt N/yr of nitrogen fixation[7] it is estimated that 79 Mt N/yr results from the synthesis of nitrogen fertilizer and the cultivation of legumes and another 21 Mt N/yr is fixed as $NO_x$ by combustion, another source puts this at 26 Mt N/yr.[28] These fixation processes have been increased rapidly in the last three decades so that between 1/4 & 1/2 of the total global rate of nitrogen fixation is due to anthropogenic activities. As part of the nitrogen cycle this leads to release of gases as shown;




thus

$$\alpha = \frac{[N_2O]}{[N_2] + [N_2O] + \frac{1}{2}[NO]}$$

In soils $\alpha$ varies widely as temperature, pH, moisture and the availability of oxygen change. Typical ranges for these parameters are

| | |
|---|---|
| land | $0.025 < \alpha < 0.1$ |
| ocean | $0 < \alpha < 1$ |
| global | $0.025 < \alpha < 0.4$ |

As little as 1% or as much as 75% of the N added via fertilizers can be lost in a few weeks. The average is in the range of 10 to 15%.

The time between fixation and denitrification can vary widely. It can be as short as hours and as long as decades. Liu et al[9] observe that it is possible that due to these long lifetimes that it may require hundreds of years for man to have a significant impact on the amount of $N_2O$ released

from the large global reservoir. Their conclusion is based on the fact that the global reservoir of fixed nitrogen is estimated to be $2 \times 10^5$ Mt so that adding even as much as 200 Mt by the year 2000 will be only a very small contribution. However McElroy et al[28] point out that in general agricultural life times are much shorter.

The rate at which nitrogen is retained in living plants is directly affected by their life cycle. For cereal crops and leaves of trees the lifetime is one year while the average time nitrogen is retained in living plants is of the order of 15 years.[9] It is generally felt that in the natural nitrogen cycle the rate of denitrification equals the rate of retention.[8] However the increase of anthropogenic $N_2O$ may upset the equilibrium.

The production, $\Delta P_{N_2O}$, of nitrous oxide is: (where $P_{N_2O}$ is the global rate of production)

$$\Delta P_{N_2O} = \alpha \beta \Delta N F$$

Where $N_F$ is the global rate of nitrogen fixation. The change in the $N_2O$ inventory must equal the difference between the production rate and the destruction rate.

$$\frac{d[N_2O]}{dt} = P_{N_2O} - \frac{[N_2O]}{\tau}$$

and when a steady state is acheived

$$[N_2O] = \tau \; P_{N_2O}$$

It is thought that at present the situation is close to steady state.

Consider now the situation where the global rate of production of nitrous oxide is increased from $P_{N_2O}$ to $P_{N_2O} + \Delta P_{N_2O}$ and kept here for a time long compared to the atmospheric residence time. A new steady state inventory will be achieved. If the change is small the new inventory will be $(P_{N_2O} + P_{N_2O})\ \tau$.

The relationship between the production of $N_2O$ and fixation of nitrogen is quite complex. However a first order approximation may be made using the expression mentioned above.

$$\Delta P_{N_2O} = \alpha \beta \Delta N_F$$

Where $N_F$ is the natural (background) global rate of fixation of nitrogen. Substituting this expression and $P_{N_2O} = [N_2O]\ \tau$ in the above yields.

$$\frac{\Delta [O_3]}{[O_3]} = X \quad \frac{\Delta [N_2O]}{[N_2O]} = X \quad \frac{\Delta P_{N_2O}}{P_{N_2O}} = X \frac{\Delta N_F}{[N_2O]} \propto \beta\tau$$

The natural global inventory [$N_2O$] is known to be about 1500 Mt N

Assume that the rate of anthropogenic fixation of nitrogen is 100 Mt N/yr (this is the increase $N_F$ over the natural rate of fixation) then

$$\frac{\Delta[O_3]}{[O_3]} = X \quad \frac{100}{1500} \alpha \beta \tau$$

If we assume that all the fixed nitrogen is denitrified in a few decades then $\beta = 1$. Using $\tau = 150$ yrs. and $\alpha = 0.1$ and assuming that $X = 1/100$ then

$$\frac{\Delta[O_3]}{[O_3]} = 0.01$$

or the ozone concentration would increase by 1%.

Some support that the increased $N_2O$ production will deplete stratospheric $O_3$ is found in the phenomena that followed a large solar proton event that occurred in the stratosphere in 1972.[54] The proton event produced NO in the stratosphere that led to a 20% decrease in stratospheric ozone at that time.

## VI. Conclusion

A broad and general conclusion regarding the ozone depleting capability of anthropogenically produced nitrous oxide emerges from the preceding analysis. There is a problem which may be very important on the time scale of 20-50 years. The problems could be a serious one but it is not an immediate crisis.

### Recommendations

The two main areas that need further study are

1. a more accurate determination of estimated global flux from soil/fertilizer/crop systems

2. a determination of how much (if any) the $N_2O$ atmospheric concentration is changing.

The role of $N_2O$ in nitrogen cycle has been the subject of much study in recent years. Although $N_2O$ rates have been deduced from these studies, much more specific information is needed to determine with some reasonable accuracy the role of each source in the overall cycle and thus its ultimate effect or stratospheric ozone. Perhaps the most important information that is needed is to know under what conditions $N_2O$ is released from soil and also how that is related to

the amount of and type of fertilizer and how it is used. These studies should be conducted in natural field conditions. Also the variation of the $N_2O/N_2$ ratio for different crops, soils and growing conditions needs to be determined. The magnitude of $N_2O$ release must be measured in the field and under different conditions of moisture, weather, soil pH, type of ground cover and type of soil.

A long term (perhaps 10 yrs) study should be made of atmospheric nitrous oxide to determine if it is changing. In particular any possible change in the quantity of nitrous oxide reaching the stratosphere needs to be determined.

With regard to possible future ocean studies it was observed that some more coverage is needed. Particularly the following areas should be sampled include: the upwelling areas of western Africa and the eastern coasts of most continents and the eastern tropic areas of the Pacific Ocean.

Also more studies should be made of fresh waters. It was noted that the Panama Canal showed high values for $N_2O$ and this suggests a study of tropical inland waters (a study of the Amazon River is planned in the near future).

In view of the studies of exhaust stack concentrations of $N_2O$ from fossil fuel power plants it would seem advisable to

monitor those in a more careful and complete way. Care should be taken concerning where the sample is collected from and what possible reactions could produce or consume nitrous oxide. A similar study should be made of exhaust gases from automobiles with catalytic converters.

Since the contributors to the knowledge and understanding of global nitrous oxide fluxes are from diverse disciplines, a symposium or workshop would be important and valuable, perhaps every 2 years. The major workers appear to be from the areas of atmospheric chemistry, atmospheric physics, oceanography, microbiology and soil sciences. It is essential that there be direct communication between workers in these diverse areas.

Other potentially sizable sources of $N_2O$ such as sewage treatment plants and feedlots need to be monitored.

Should cultivation and fertilizer practices be changed? It appears that anthropogenic sources of $N_2O$ can have a sizeable effect on stratospheric ozone. The most important of these contributions involve planting, cultivating and fertilizing crops. The implications of the problem on world food production is immense and beyond the present analysis. However it can be seen that political and economic decisions in the not to distant future will require a better knowledge of the impact

of nitrous oxide of stratospheric ozone than is now known. Some continued and new studies, investigations and monitoring are clearly indicated.

## Appendix

### IMPORTANT NUMERICAL DATA FOR $N_2O$

| | |
|---|---|
| Tropospheric Burden | $1.7 \times 10^{15}$ gm |
| Stratospheric Burden | $0.17 \times 10^{15}$ gm |
| Residence Time | 100 - 150 years |
| Guesstimate of Global Flux | $210 \times 10^{12}$ gm $N_2O$/yr |
| Soil Flux | $0.1 - 3.4 \times 10^{-12}$ gm $cm^{-2} s^{-1}$ |
| Land Flux | up to $40 \times 10^{-12}$ gm $cm^{-2}$ $s^{-1}$ |
| Water Flux | $\sim 2 \times 10^{-12}$ gm $cm^{-2}$ $s^{-1}$ |
| Oceans | $.82 - 1.66 \times 10^{-12}$ gm $cm^{-1}$ $s^{-1}$ |
| Fertilizer $N_2O$ | 5-20% |
| Area of: freshwater | $2 \times 10^{16}$ $cm^2$ |
| forests | $4.1 \times 10^{17}$ $cm^2$ |
| unused land | $4.9 \times 10^{17}$ $cm^2$ |

From Crutzen[11]

- deposition velocity = $\frac{\text{atmospheric scale height}}{\text{atmospheric residence time}} = \frac{8.5 \text{ km}}{10 \text{ yr.}}$

$= 2.7 \times 10^{-3}$ cm $sec^{-1}$

- flux of $N_2O$ into stratosphere = 9 Mt N/yr.

$= 1.2 \times 10^{9}$ molecules $cm^{-2}$ $s^{-1}$

Atmospheric concentration of 0.3 ppm v is equivalent to a concentration in the soil of 0.013 µg $N_2O$-N/g[31]

$10^{12}$ gm = 1 Mt (million metric tons) = $10^6$ tonnes

1 ha = $10^4$ $m^2$

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